

**CHEMICAL SENSING OF UNEXPLODED ORDNANCE
WITH THE
MOBILE UNDERWATER SURVEY SYSTEM (MUDSS)**

M. R. Darrach, A. Chutjian

Jet Propulsion Laboratory, California Institute of Technology
4800 Oak Grove Drive
Pasadena, CA 91109 USA

Abstract

The ability to sense explosives residues in the marine environment is a critical tool for identification and classification of underwater unexploded ordnance (UXO). Trace explosives signatures of TNT and DNT have been extracted from multiple sediment samples adjacent to unexploded undersea ordnance at Halifax Harbor, Canada. The ordnance was hurled into the harbor during a massive explosion fifty years earlier, in 1945 after World War II had ended. Laboratory sediment extractions were made using the solid-phase microextraction (*SPME*) method in seawater, and detection using the Reversal Electron Attachment Detection (*READ*) technique and, in the case of DNT, a commercial gas-chromatography/mass spectrometer (*GC/MS*). Results show that, after more than 50 years in the environment, ordnance which appeared to be physically intact gave good explosives signatures at the parts-per-billion level, whereas ordnance which had been cracked open during the explosion gave no signatures at the 10 parts-per-trillion sensitivity level. These measurements appear to provide the first reported data of explosives signatures from undersea UXOs.

I. Introduction

The detection of undersea UXOs is a matter of vital concern to several United States agencies, including the Department of Defence (US Navy, Army Corps of Engineers), and the Environmental Protection Agency. This issue has been highlighted as a result of the Base Realignment and Closure (BRAC) Act in which formerly-used defense sites (FUDS) will be returned to the civilian sector.

Central to the problem of undersea UXOs is their detection, by both physical means (*e.g.*, forward- and side-scanning sonars, magnetic-field gradiometers, electro-optical sensors) and chemical means (*e.g.*, seawater and/or sediment sampling and detection). A suite of these physical and chemical sensors has been incorporated into the so-called Mobile Undersea Debris Survey System (MUDSS) (1). The present study is aimed at testing the hypothesis that sediment sampling near a UXO, followed by chemical extraction and detection, can be a viable method of verifying an active target. To our knowledge, this is the first chemical evaluation under actual environmental conditions of sediment adjacent to old, live UXOs (2).

The site chosen for the sediment sampling was offshore of Rent Point in Halifax Harbor, Canada. On a historical note Halifax, Nova Scotia was a nexus for convoys destined for Europe during the Second World War. When the war ended, ships returning from Europe unloaded live ordnance of every type. A minor fire in 1945 caused detonation of the storage complex and for ten days explosions scattered large quantities of UXOs. After the explosions subsided a modest cleanup was pursued on land and the nearby shoreline was restricted to military personnel, leaving underwater UXOs undisturbed for 50 years. Hence all of the ordnance at Halifax could be expected to be live, with few if any inert rounds

The samples were brought back to the laboratory, and any explosives materials extracted using solid-phase microextraction (*SPME*). The extracted species were detected using the Reversal Electron Attachment Detection (*READ*) technique and, for verification in some cases, a commercial gas-chromatography/mass spectrometer (*GC/MS*). The *READ* system uses the fact that explosives have an extremely large cross section for attachment of zero-energy electrons, *via* the so-called *s*-wave attachment phenomenon. The *SPME/READ* technique is highly selective towards those molecules which adsorb to the *SPME* fiber, and have large electron attachment cross sections at ultralow electron energies. Its use as opposed to, for example, use of more accessible *GC/MS* or *HPLC/MS* methods, offers the possibility of good selectivity, free of interferences from other chemical species present in sea water

II. EXPERIMENTAL

Sediment Acquisition Procedure

A site off Rent Point in the Bedford Basin, adjacent to the ammunition-storage bunkers used by the Canadian Armed Forces was chosen for collection of the samples. The services of the Harbor Inspection Dive Team of the Canadian Armed Forces Reserves were generously provided for the hazardous task of UXO sediment collection. The dive team first surveyed a portion of the seabed, locating, marking, and videotaping the target UXOs. After the dive team returned to shore the videotape was reviewed to identify which UXOs should be sampled. This judgement was based on whether the UXO was intact, or was broken open. Then the dive team returned to each targeted UXO and acquired sediment samples at distances of between 6-12" from the UXO. One sample was taken from each of four cardinal points around each UXO. This process was also videotaped. The total sample collected was 250 ml of a sediment-water slurry for each target. Finally, the samples were returned to the surface and labeled. Samples obtained the first day remained at ambient temperature for no longer than 6 h before being placed in a commercial freezer after the day's collection was completed. The holding times of nitroaromatic and nitramine explosives in water have been studied extensively (3), and it is found that trace explosives can be up to 90 days provided the samples are stored in silanized containers and frozen immediately after collection.

Explosives-Sediment Extraction Procedure

Considerable work has been carried out at several laboratories on characterizing the dissolution and extraction of explosives in seawater and ground soil (4). Based on these results the extraction procedure here was sonication for at least 1 hour of the sediment sample after the addition of 100 ml methanol or acetonitrile. At the end of sediment sonication, soil and liquid layers were allowed to separate and the liquid layer pipetted into a separate, clean silanized glass beaker. The glass beakers containing the pipetted water/solvent mixture were then desiccated inside a vacuum bell jar connected to a dry-ice cooled cold trap. After desiccation was complete 250 ml water was added to each sample, and the sample sonicated for an additional 1 hour.

Results indicate that three methods are effective in extracting explosives from solutions in water (5). These methods are (a) solid-phase extraction (*SPE*), (b) salting-out solvent extraction (*SOE*), and (c) membrane *SPE*. For this investigation the extraction of explosives from the aqueous solution was effected by solid-phase microextraction (*SPME*). The poly(dimethylsiloxane) divinylbenzene (PS-DVB) fiber used in the *SPME* has been found to have the highest relative efficiency of the commercially-available fibers for TNT extraction. A bubble aeration scheme was used to agitate the sample during *SPME* extraction which enhanced extraction efficiencies and hence reduced extraction time, and eliminated losses through adsorption of trace explosives to a stir bar. Equilibrium times for the adsorption of explosives to the *SPME* fiber were found to be approximately 5 min.

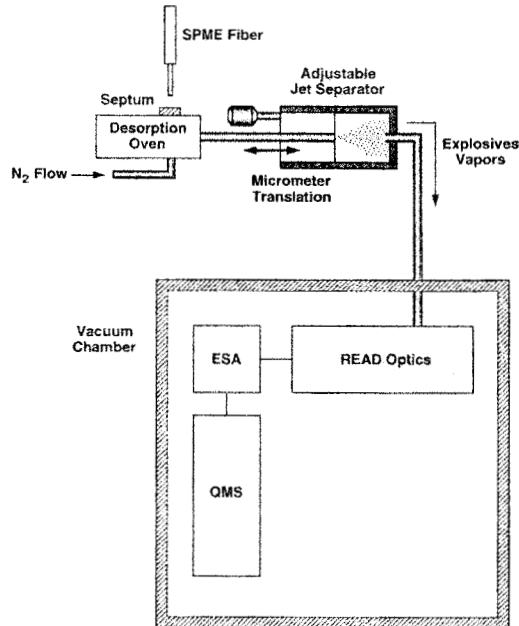


Figure 1. Schematic diagram of the *SPME/READ* system used in this study. Electron reversal and attachment, and ion extraction take place within the *READ* optics. The electrostatic analyzer (*ESA*) ensures the sign of charge by deflecting the negative ions after attachment in the *READ* optics to the quadrupole mass spectrometer (*QMS*).

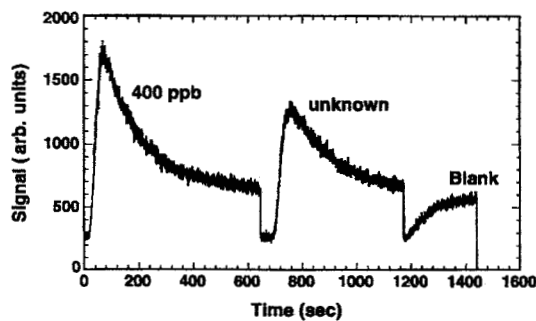


Figure 2. Display of the *SPME/READ* TNT negative-ion fragment signal at $m/e = 167$ u. Time is shown after injection of extractions from a 400 ppb standard TNT solution, a sediment-extraction sample of unknown concentration, and a blank.

As an independent test of the *SPME/READ* analysis, the solvent-extracted material from three different sediment samples were split and analyzed by *GC/MS* for the presence of trace TNT or DNT. The *GC/MS* results obtained from analysis of the sediments are summarized in Table 1.

In general, the results herein indicate that sediment collected near UXOs that appeared (through visible inspection) to be broken open showed *no* evidence for TNT. Ultimate detection sensitivities of 10 ppb were observed for TNT in water. Samples near targets that appeared intact showed trace explosives up to parts-per-billion concentration levels. For the intact rounds, positive results were found at only two of the four cardinal points, indicating a directionality to the source. *Intact* munitions appear to be releasing their contents as a slow leak, very likely through pinholes in the eroded casing, or through the screw threads linking the fuse assembly to the main charge. Presumably, the signal strength is

Since RDX explosives charges had been used in Halifax Harbor to effect an initial cleanup of the UXOs, it was decided not to test the samples for trace RDX: positive results for RDX could almost certainly be ascribed to residues of the cleanup. Also, present within the collected sediment were numerous fragments of cordite. Cordite was commonly used during World War II as the propellant charge in artillery rounds. It was typically composed of a mixture of nitrocellulose, nitroglycerin and lubricants. Because of the high selectivity of the *READ* detection system to TNT, RDX, PETN, *etc.* (see below) no false positive results were expected, or found, due to the cordite in the sediment. To test that this propellant could not yield false positives a two-gram piece of cordite was placed in a passivated beaker with 250 ml of water. The beaker was placed in a sonic bath for about 1 hour and an *SPME* extraction from the aqueous solution performed. No mass peaks which would interfere with identification of TNT or DNT were observed.

The *READ* System Used With *SPME*

Details of the operation of the *READ* have been given elsewhere and its operation with explosives discussed (6-8). Briefly, the *READ* system uses the fact that the explosives molecules have an extremely large cross section for attaching zero-energy electrons. This cross section varies as (electron velocity)⁻¹. Hence the attachment rate (or ionization efficiency) is favored for slow electrons. Referring to the block diagram in Fig. 1, the *READ* system provides a large density of electrons with zero- and near-zero velocities by stopping and reversing, using a shaped electrostatic mirror, the current from an electron gun column. The analyte is introduced to this stopping region, and upon attachment each explosives type forms a characteristic negative-ion fragmentation pattern. Using a quadrupole mass spectrometer, the *READ* monitors one or more fragment peaks to detect the species, and with calibration to provide concentration levels. The explosives molecules are thermally desorbed from the *SPME* fiber by injection into an oven connected to the *READ* where the explosive vapors pass through the gas line into an adjustable jet separator and then into the *READ*. The desorption oven and gas line are typically maintained at 190 C and the jet separator at 140 C during operation. No evidence for deterioration of the explosives at these temperatures was found.

Results and Discussion

Shown in Fig. 2 is the time evolution of the fiber desorption where the mass peak $m/e = 167$ *u* of TNT is monitored. Typically, an *SPME* extraction of a sediment sample was sequentially analyzed with *SPME* extractions of a spiked sample of known concentration, then a seawater blank. This technique enabled an accurate determination of the trace explosives yields with no effects due to possible instrumental drifts. The *SPME* results for the sediments collected near the Halifax UXOs are summarized in Table 1. The negative-ion signal detected by the *SPME/READ* system as a function of calibrated samples of TNT in water is shown in Fig 3. A new *READ* device is currently undergoing testing which will improve the sensitivities by a factor of at least 100.

strongest near the point of emission, hence the directionality within the sediment samples. This directionality could be assisted by a prevalent, directed bottom current. One may also presume from the detection results that, in the fifty years since the Halifax explosion, *broken* munitions have had their contents dissolved, reacted, biodegraded or even photodegraded. One may also conclude that trace explosives can very likely be detected at even *further distances* from a UXO, certainly with diminished concentration levels but well within present *SPME/READ* detection limits.

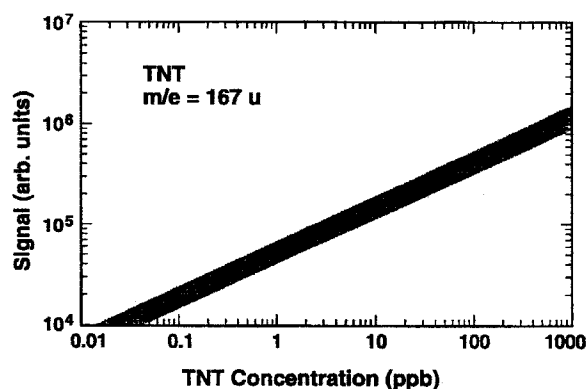


Figure 3. Sensitivity curve of the *SPME/READ* system to TNT concentration in water ($m/e = 167\ u$ monitored). The shaded region represents the sensitivity, and its error, in determining the TNT concentration corresponding to the indicated signals.

It is clear that in any UXO disposal strategy one would gain further information about a UXO site from chemical examination of the sea-bottom sediments. This additional information be expected to yield positive results. Hence the chemical information offers another diagnostic dimension which is quite orthogonal to that from optical, magnetometer, and sonar instruments which are presently being deployed for UXO detection and classification. Chemistry will be an important tool in any explosives-ordnance disposal strategy.

Acknowledgements

The authors would like to acknowledge the excellent cooperation and assistance of LCDR J. Hewitt, Commanding Officer of the Fleet Diving Unit/Atlantic; and of the Harbor Inspection Dive Team of CFB Shearwater, Nova Scotia, Canada. This work was performed at the Jet Propulsion Laboratory, California Institute of Technology, and was supported by the Office of Naval Research, and the Department of Defense/Strategic Environmental Research and Development Program through agreement with the National Aeronautics and Space Administration.

Table 1. Summary of the SPME/READ Explosives Tests on Samples Collected at Halifax, Nova Scotia, Canada.

Target Number	Target Description	Sample Identification	Results
1	5" shell, poor condition broken open	A, B, C, D	no explosives detected
2	5" shell, very poor condition broken open	E, F, G, H	no explosives detected
3	5" shell, good condition intact	I, J	no explosives detected (confirmed by GC/MS)
		W, X	TNT detected at low ppb concentrations
4	9" shell, semi-buried appeared intact	K, L	DNT detected at high ppb concentrations
		M, N	no explosives detected
5	5" shells, very poor condition broken open	O, P, Q, R	no explosives detected (confirmed by GC/MS)
6	5" shell, semi-buried intact	T	DNT detected at low ppb concentrations (confirmed by GC/MS)
		S, U, V	no explosives detected (confirmed by GC/MS)
7	background sediment sample	17, 20	no explosives detected

Literature Cited

1. The MUDSS is a JPL-USN Coastal Systems Station collaboration sponsored under the Department of Defense/Strategic Environmental Research and Development Program (SERDP).
2. See also, for example, Fauth, M. I. *Determination of the Fate of Fragmented or Unexploded Munitions and Munitions Ingredients in the Environment* □ a Literature Search, DTIC AD-B120489(L) C.1 (1988).
3. Grant, C. L.; Jenkins, T. F.; Meyers, K. F.; McCormick, E. F. *Env. Toxic. Chem.* **1995**, *14*, 1865.
4. Bruggemann, E. E. *HPLC Analysis of SEX, HMX, TAX, RDX and TNT in Wastewater*; Army Medical Bioengineering Research and Development Laboratory, Report USAMBRDL-TR-8206; Fort Detrick, MD, 1983.
5. Jenkins, T. F.; Miyares, P. H.; Meyers, K. F.; McCormick, E. F. *Anal. Chim. Acta* **1994**, *289*, 69.
6. Bernius, M. T.; Chutjian, A. *Anal. Chem.* **1990**, *62*, 1345.
7. Boumsellek, S.; Chutjian, A. *Anal. Chem.* **1992**, *64*, 2096.
8. Boumsellek, S.; Alajajian, S. H.; Chutjian, A. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 243.